

ANALYTICAL PYROLYSIS OF COAL
DEVELOPMENT OF A THERMAL DEGRADATION PROFILE

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The challenge to obtain comprehensive analytical information on fossil fuels has led to the development of advanced methods in analytical pyrolysis. Extension of material science characterization techniques to coal and shales has permitted compositional data (elemental and structural) to be obtained on the solid and generated volatiles. CDS instrumentation has been successfully applied in both material sciences (1) and fossil fuel studies (2-4) with emphasis on the simulation of process conditions coupled to on-line gas chromatographic (GC) analysis. Analytical pyrolysis coupled with advanced concentrator technology is now applied to fossil fuels to provide a more complete range of information in a cost-effective manner.

Development of a thermal degradation profile involves application of controlled thermal inputs under inert and reactive atmospheres within the range of realistic process conditions. Experimental design for the coal and shales has utilized the Pyroprobe 123 system coupled to a modern GC unit with capillary column capabilities. Evolved volatiles are produced from either pulsed pyrolysis or programmed heating throughout chosen temperature intervals between 100-1000°C. Both inert and reactive atmospheres influence the nature and amount of evolved volatiles. The latter are trapped on a concentrator trap that is integral to the 123 system; the volatiles are then thermally desorbed as a sharp pulse into the GC. Since these data are obtained from weighed (milligram) amounts of coal shale samples, mass balance calculations may be obtained under the full range of imposed thermal/reactive treatments.

Figure 1 shows the FID/GC chromatogram of volatiles evolved from 5 mg of coal under an (a) oxidative (air) and (b) inert (helium) atmosphere in the low-temperature range (held at 275°C for 10 minutes). This analysis of the volatiles illustrates the type of GC pattern which, when coupled with identification and quantitation, provide the needed detailed structural information. Selected reference compounds and internal standardization procedures allow specific monitoring of substances and their fate under the chosen conditions, i.e. water, entrapped gases, etc.

In addition to the low-level thermal processing of fossil fuel samples under inert, oxidation, or reductive atmospheres, higher temperatures at varying rates may be imposed upon the samples. In Figure 2, pyrolysis patterns are shown from a coal sample treated at 60°/min to 1000°C for 32 min. under an (a) air and (b) helium atmosphere. The evolved volatiles were collected in the internal Tenax trap and subsequently thermally desorbed into the capillary GC system under the conditions given in Table 1. Other workers have shown that 1-alkene/alkane ratios are correlated to process yields from oil shales (5).

Previous studies in material sciences with complex polymer formulations for smoke, flammability, and toxicity studies have also shown that oxidative thermal treatments markedly alter the generation and reaction of polyenyl free-radicals in the solid phase (6). Certain organic/inorganic matrices produce increased cross-linking and char when pyrolyzed under oxidative (combustive) atmospheres, while increased chain-scission and greater volatilization resulted from degradation under inert (pyrolytic) atmospheres. Conjugated aromatic structures are dramatically affected by these factors.

Further studies to control and optimize the thermal degradation pathways of complex organic systems have shown that certain inorganic additives are very effective. The role of transition-metal compounds has been studied extensively (7) as smoke suppressant additives that promote extensive cross-linking in the solid phase by a proposed "reductive coupling" mechanism (7b). Hence, screening of such additives to effect the desired chain-scission and volatilization is directly accomplished by the analytical pyrolysis method. Thereby, addition of selected inorganics or organometallics to the coal or shale matrix permits optimization of degradation pathways in coal gasification, denitrification, or desulfurization processes. Illustrations will be shown to demonstrate this role of analytical pyrolysis.

Finally, in concert with the detailed monitoring of key products and the chromatographic patterns as a function of these thermal/reactive treatments, the overall elemental composition of coal and shales is important data. A unique capability of CDS instrumentation is shown in Figure 3 with the simultaneous determination of CHNS content of a typical coal sample. This analysis is accomplished by on-line reaction GC to effect standard microchemical conversions of the volatiles generated from the coal sample (heated to 1300°C in oxygen). With such data, effective N or S removal treatments may be monitored in concert with the volatile composition, since only a few milligrams are needed for these analyses.

In summary, it can be demonstrated that valuable information is generated in laboratory scale by simulation and analysis of realistic process variables of temperature, atmosphere, and catalytic additives. This data should aid on-going coal conversion process technologies as the thermal degradation profile is further developed.

References

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Table 1

320 Concentrator

Sample: 5 mg coal in quartz tube/coil
Pyroprobe
Sampling: Desorber Purge 1 min., no heat
Desorber Heat 250°C for 15 min.
24" x 1/8" OD SS Tenax Trap -
20 ml/min He (or air)
Injection: Backflush Trap A at 60 ml/min.
He (split flow) at 265°C for 5
min to GC
Recondition: Backflush Trap A at 25 ml/min
He at 265°C for 10 min.

Pyrolysis

Sampling: Pyroprobe: 1000°C at 60°/min
for 30 min
Desorber Purge 1 min, no heat
Desorber Heat 250°C for 32 min,
20 ml/min He (or air)
Injection: As above
Recondition: As above

GC Analysis - Perkin Elmer, Sigma II, FID

Column: 25 x .21 mm ID flexible fused
silica WCOT OV-101
Oven: 40°C, 2 min, then 10°/min to 275°C,
10 min
Split flow: 60 ml/min He; split ratio,
60:1
Detector: Att'n x 10⁻¹² as noted
Chart: 1 cm/min

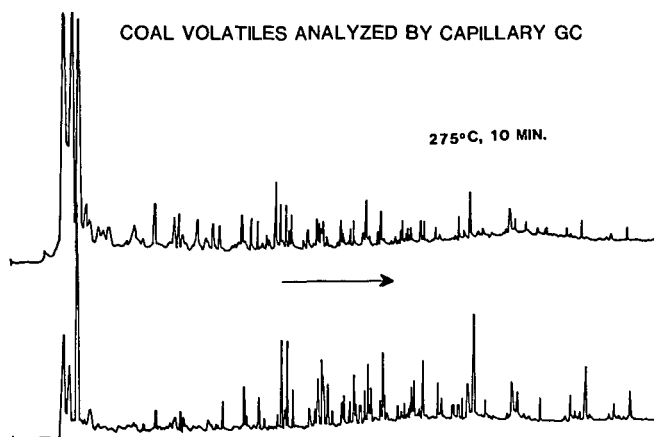


Figure 1 - Coal Volatiles Analyzed by Capillary GC - Thermal Treatment at Low Temperature (275°C, 10 min) in (a) air (b) helium

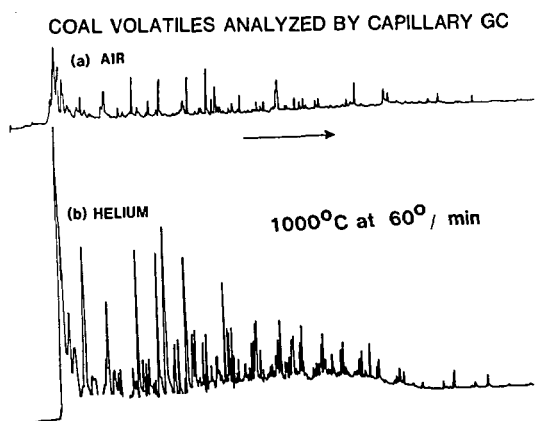


Figure 2 - Coal Volatiles Analyzed by Capillary GC - Thermal Treatment at high temperature (100° to 1000°C at 60°/min) in (a) air (b) helium

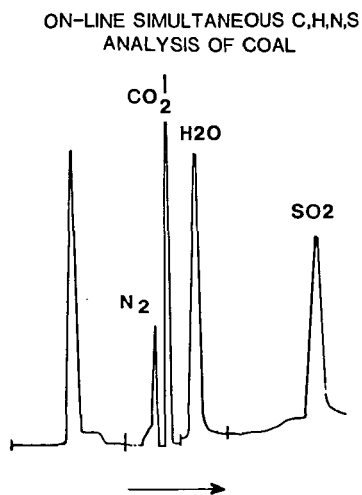


Figure 3 - On-line, Simultaneous Elemental C, H, N, S, Analysis of coal